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(54) Title: MULTI-LAYER POLYMERIC FILM

(57) Abstract: A film according to the present invention, there is provided a multi-layer laminated polymeric film comprising a substrate layer having on one side thereof a heat-scalable peelable layer and having on the opposite side thereof a shrinkable layer, wherein said shrinkable layer has a degree of shrinkage in a first dimension of about 10-80 % over the temperature range 55 to 100 °C, and a ratio of shrinkage at 100 °C said first dimension relative to a second, orthogonal dimension in the range of 1:1 to 1:1; a process for making the same; and the use of said film as a lid for a container, particularly a container used for packaging ready-prepared ovenable meals.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

MULTI-LAYER POLYMERIC FILM

This invention relates to a multi-layer polymeric film, and in particular to a laminated multi-layer polyester film which is suitable for use as a lid for a container, particularly a 5 container used for packaging ready-prepared ovenable meals.

Plastic containers have been increasingly used in packaging applications, such as food packaging, and in particular for packaging convenience foods, for example ready-prepared ovenable meals which are warmed either in a microwave oven or in a conventional oven. 10 Often the plastic container is a APET/CPET tray (a composite material having an amorphous polyethylene terephthalate layer on top of a crystalline polyethylene terephthalate layer). The use of plastic containers has led to a requirement for lids which can both seal the container, in order to prevent leakage and drying out of the packaged contents during storage, and also be easily peeled from the container on opening. The lids 15 should also not stick to the packaged contents and should be able to withstand the heat generated in the oven.

Such container lids normally comprise a film comprising a flexible substrate and a sealable coating layer, and are often referred to as "lidding" films. Oriented polymeric film, 20 particularly biaxially oriented polyester film, has previously been used as the flexible substrate for lidding films. In prior art lidding films, the heat-sealable layer is often applied to the substrate in an "off-line" coating step, i.e. after any stretching and subsequent heat-setting operation employed during the manufacture of the substrate. The heat-sealable layers of such films are generally applied using organic solvent, which is not 25 suitable for "in-line" coating, and can cause sticking or blocking of the film during the normal winding operations used during film manufacture. In addition, the organic solvents used may be harmful, hazardous in use, or toxic and detrimental to the environment.

WO-A-96/19333 discloses a lidding film produced by an in-line coating process which 30 avoids the use of substantial amounts of organic solvents. The film comprises a substrate and a coating layer of a copolyester of (a) 40 to 90 mole % of at least one aromatic dicarboxylic acid, (b) 10 to 60 mole % of at least one aliphatic dicarboxylic acid, (c) 0.1 to 10 mole % of at least one dicarboxylic acid comprising a free acid group and/or a salt

thereof, (d) 40 to 90 mole % of at least one glycol having from 2 to 12 carbon atoms, and (e) 10 to 60 mole % of at least one polyalkylene glycol. The coating layer is applied as an aqueous dispersion or solution either before the film substrate is stretched or between the stretching steps of a biaxial stretching process. The process disclosed in WO-A-96/19333  
5 is limited to certain types of coating compositions, i.e. those that are soluble or adequately dispersible in water.

The manufacture of sealed containers using such lidding films involves the formation of a seal between the lidding film and the container. This seal is formed by placing the lid on  
10 top of the container and applying heat and pressure in order to soften or melt the sealable coating layer so that it adheres to the surface of the container and forms an effective seal between the lid and the container. Unfortunately, a seal which is strong enough to prevent leakage of the contents often results in difficulties in removing the lid when the container is to be opened. In particular, the lid may tear during peeling and portions of the film lid  
15 may fall into the contents of the container thereby spoiling the food. It would be desirable to eliminate the difficulties encountered during peeling. A strong seal and easy peeling properties, i.e. a clean peel, are desirable at both low, e.g. ambient, and high temperatures, e.g. after heating the packaged food contents in an oven.  
20 A further consideration with ready-prepared convenience meals is that water vapour is driven from the food during the cooking cycle. If the steam thereby produced is not vented, the build-up of pressure may cause the film lid to burst, causing fragments of the film lid to contaminate the contents of the container. Previous film lids for ovenable ready-prepared food containers generally required that the user pierce the lid to prevent  
25 this. However, the need for piercing the lid prior to warming the food in its container is often forgotten or not understood by the user. It would be advantageous to provide a container lid which did not require the user to pierce it before cooking.

It is an object of this invention to provide an alternative lidding film which exhibits  
30 superior peeling characteristics and is self-venting.

According to the present invention, there is provided a multi-layer laminated polymeric film comprising a substrate layer having on one side thereof a heat-sealable peelable layer

and having on the opposite side thereof a shrinkable layer, wherein said shrinkable layer has a degree of shrinkage in a first dimension of about 10-80% over the temperature range 55 to 100°C, and a ratio of shrinkage at 100°C in said first dimension relative to a second, orthogonal dimension in the range from 1:1 to 10:1.

5

The film of the present invention is intended for use by heat-sealing the film onto an ovenable container. During the cooking cycle the food product contained in the sealed container heats up and steam is produced. Heat from the steam and from general radiant heat is transferred to the film lid. Once the temperature of the shrinkable layer reaches its  
10 shrink initiation temperature, it starts to shrink, thereby applying a shear force to the film lid. In addition, the strength of the heat-seal bond between the container and the film lid will start to reduce as the temperature increases, particularly when the temperature passes the glass transition temperature of the heat-seal layer polymer. As the bond between the film lid and the tray weakens, the shear force exerted by the shrinkable layer causes the lid  
15 to curl back on itself and peel open during the cooking cycle. The self-peeling lid therefore allows the venting of steam generated during the cooking cycle. This is particularly advantageous for solid foods, particularly dough-based foods such as microwaveable pizzas because it prevents the base becoming soggy or water-logged. The self-peeling lid also avoids any difficulties, such as tearing of the film lid, which are  
20 associated with opening of the container by the user once the cooking cycle is complete.

A multi-layer laminated film according to the present invention typically exhibits a heat-seal value (at ambient temperatures) in the range of 200 to 1400g/25mm<sup>2</sup>, preferably in the range of about 200 to about 1000g/25mm<sup>2</sup>, when sealed to a standard APET/CPET tray.  
25 Typical heat seal strengths of the film to itself are in the range of 600-800g/25mm<sup>2</sup>.

The thickness of the multi-layer laminated film is preferably between about 20 to 250 µm, more preferably between about 40 and 100 µm, and typically is about 60-80 µm in thickness.

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The primary characteristic of the lidding film of the present invention is that it exhibits self-peeling during the cooking cycle. In order for this to occur, the shrinkable layer must

have a degree of shrinkage in a given dimension that is greater than the degree of shrinkage of the substrate layer in that dimension.

As the skilled person is aware, the shrinkage characteristics of a film are determined by the 5 stretch ratios and degree of heat-setting employed during its manufacture. The shrinkage behaviour of a film which has not been heat-set corresponds to the degree to which the film has been stretched during its manufacture. In the absence of heat-setting, a film which has been stretched to a high degree will exhibit a high degree of shrinkage when subsequently exposed to heat; a film which has only been stretched by a small amount will only exhibit a 10 small amount of shrinkage. Heat-setting has the effect of providing dimensional stability to a stretched film, and "locking" the film in its stretched state. Thus, the shrinkage behaviour of a film under the action of heat depends on whether, and to what extent, the film was heat-set after the stretching operation(s) effected during its manufacture. In general, a film which has experienced a temperature  $T_1$  during the heat-setting operation will exhibit 15 substantially no shrinkage below temperature  $T_1$  when subsequently exposed to heat after manufacture.

Accordingly, in order that the shrinkable layer exhibit the required shrinkage characteristics in the final laminated film, it is preferred that the shrinkable layer is not 20 heat-set after stretching has been effected. However, the skilled person will recognise that films according to the present invention may also be produced using shrinkable layers which have been partially heat-set.

In a preferred embodiment, the substrate layer is a dimensionally stable film which exhibits 25 substantially no shrinkage under the action of heat, and the shrinkable layer is a layer which shrinks in one dimension under the action of heat. The film lid of this embodiment, under the action of heat, therefore peels back on itself in one direction only. In this preferred embodiment, the substrate layer may be a biaxially-oriented heat-set polymeric layer and the shrinkable layer may be a uniaxially-oriented layer which has not been heat- 30 set.

As the skilled person is aware, the dimensions of a polymeric film are defined in terms of the "machine direction" and the "transverse direction", which correspond to the axes of the

film production apparatus. The machine direction is the direction of travel along the film production line and corresponds to the lengthways dimension of the film. The transverse direction is the direction orthogonal to the direction of travel of the film during manufacture and corresponds to the widthways dimension of the film. Conveniently, the  
5 shrinkable layer of the preferred embodiment described above exhibits uniaxial shrinkage in the transverse direction.

- The present invention is not limited, however, to films which shrink in only one dimension. For instance, the shrinkable layer may shrink in a first dimension as well as in  
10 a second, orthogonal dimension. The degree of shrinkage in one dimension may be the same as, or different to, the degree of shrinkage in the second, orthogonal direction. Thus, in an alternative embodiment, the substrate layer is a dimensionally stable film which exhibits substantially no shrinkage under the action of heat, and the shrinkable layer is a layer which shrinks in two dimensions under the action of heat. The film lid of this  
15 embodiment, under the action of heat, therefore peels back on itself in two directions. In this preferred embodiment, the substrate layer may be a biaxially-oriented heat-set polymeric layer and the shrinkable layer may be a biaxially-oriented layer which has not been heat-set.
- 20 The present invention is also not limited to films in which the substrate exhibits substantially no shrinkage. For instance, the substrate may also exhibit shrinkage in one or two dimensions provided that the degree of shrinkage of the substrate layer in a given dimension is less than the degree of shrinkage of the shrinkable layer in that dimension. Thus, in an alternative embodiment the substrate layer and the shrinkable layer may be  
25 layers which have different compositions and/or have been produced using different manufacturing conditions (such as different stretch ratios and/or heat-set processing conditions) and which therefore have different relative degrees of shrinkage in a given dimension.
- 30 The respective layers of the multi-layer laminated film are described in more detail below.

The Substrate Layer

The substrate is a self-supporting film or sheet by which is meant a film or sheet capable of independent existence in the absence of a supporting base. The substrate may be formed from any suitable film-forming material. Thermoplastic polymeric materials are preferred.

- 5 Such materials include a homopolymer or copolymer of a 1-olefin, such as ethylene, propylene and but-1-ene, a polyamide, a polycarbonate, PVC, PVA, polyacrylates, celluloses and particularly a synthetic linear polyester.

The synthetic linear polyesters useful as the substrate may be obtained by condensing one  
10 or more dicarboxylic acids or their lower alkyl (up to 6 carbon atoms) diesters, eg terephthalic acid, isophthalic acid, phthalic acid, 2,5-, 2,6- or 2,7-naphthalenedicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, 4,4'-diphenyldicarboxylic acid, hexahydro-terephthalic acid or 1,2-bis-p-carboxyphenoxyethane (optionally with a monocarboxylic acid, such as pivalic acid) with one or more glycols, particularly an  
15 aliphatic or cycloaliphatic glycol, e.g. ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol and 1,4-cyclohexanedimethanol. An aromatic dicarboxylic acid is preferred. An aliphatic glycol is preferred.

In a preferred embodiment, the polyester is selected from polyethylene terephthalate and  
20 polyethylene naphthalate. Polyethylene terephthalate (PET) is particularly preferred.

The substrate may also comprise a polyarylether or thio analogue thereof, particularly a polyaryletherketone, polyarylethersulphone, polyaryletheretherketone, polyaryletherethersulphone, or a copolymer or thioanalogue thereof. Examples of these  
25 polymers are disclosed in EP-A-001879, EP-A-0184458 and US-4008203. Blends of such polymers may also be employed. Other thermoset resin polymeric materials suitable for use as the substrate include addition-polymerisation resins, such as acrylics, vinyls, bis-maleimides and unsaturated polyesters; formaldehyde condensate resins, such as condensates with urea, melamine or phenols, cyanate resins, functionalised polyesters,  
30 polyamides or polyimides.

The substrate may comprise one or more discrete layers of the above film-forming materials. The polymeric materials of the respective layers may be the same or different.

For instance, the substrate may comprise one, two, three, four or five or more layers and typical multi-layer structures may be of the AB, ABA, ABC, ABAB, ABABA or ABCBA type. Preferably, the substrate comprises only one layer.

- 5 Formation of the substrate may be effected by conventional techniques well-known in the art. Conveniently, formation of the substrate is effected by extrusion, in accordance with the procedure described below. In general terms the process comprises the steps of extruding a layer of molten polymer, quenching the extrudate and orienting the quenched extrudate in at least one direction.

10

- The substrate may be uniaxially-oriented, but is preferably biaxially-oriented, as noted above. Orientation may be effected by any process known in the art for producing an oriented film, for example a tubular or flat film process. Biaxial orientation is effected by drawing in two mutually perpendicular directions in the plane of the film to achieve a  
15 satisfactory combination of mechanical and physical properties.

- In a tubular process, simultaneous biaxial orientation may be effected by extruding a thermoplastics polyester tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which  
20 will induce longitudinal orientation.

- In the preferred flat film process, the substrate-forming polyester is extruded through a slot die and rapidly quenched upon a chilled casting drum to ensure that the polyester is quenched to the amorphous state. Orientation is then effected by stretching the quenched extrudate in at least one direction at a temperature above the glass transition temperature of the polyester. Sequential orientation may be effected by stretching a flat, quenched extrudate firstly in one direction, usually the longitudinal direction, i.e. the forward direction through the film stretching machine, and then in the transverse direction. Forward stretching of the extrudate is conveniently effected over a set of rotating rolls or  
25 between two pairs of nip rolls, transverse stretching then being effected in a stenter apparatus. Stretching is effected to an extent determined by the nature of the polyester, for example polyethylene terephthalate is usually stretched so that the dimension of the oriented film is from 2 to 5, more preferably 2.5 to 4.5 times its original dimension in the  
30

or each direction of stretching. Typically, stretching is effected at temperatures in the range of 70 to 125°C. Greater draw ratios (for example, up to about 8 times) may be used if orientation in only one direction is required. It is not necessary to stretch equally in the machine and transverse directions although this is preferred if balanced properties are  
5 desired.

A stretched film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint at a temperature above the glass transition temperature of the polyester but below the melting temperature thereof, to induce crystallisation of the  
10 polyester. The actual heat-set temperature and time will vary depending on the composition of the film but should not be selected so as to substantially degrade the tear resistant properties of the film. Within these constraints, a heat set temperature of about 135° to 250°C is generally desirable, as described in GB-A-838708.

15 Where the substrate comprises more than one layer, preparation of the substrate is conveniently effected by coextrusion, either by simultaneous coextrusion of the respective film-forming layers through independent orifices of a multi-orifice die, and thereafter uniting the still molten layers, or, preferably, by single-channel coextrusion in which molten streams of the respective polymers are first united within a channel leading to a die  
20 manifold, and thereafter extruded together from the die orifice under conditions of streamline flow without intermixing thereby to produce a multi-layer polymeric film, which may be oriented and heat-set as hereinbefore described. Formation of a multi-layer substrate may also be effected by conventional lamination techniques, for example by laminating together a preformed first layer and a preformed second layer, or by casting, for  
25 example, the first layer onto a preformed second layer.

The substrate layer is suitably of a thickness between about 5 and 350µm, preferably from 9 to about 150µm and particularly from about 12 to about 40µm.

30 The Heat-Sealable Peelable Layer

The heat-sealable layer is any layer capable of forming a heat-seal bond to the surfaces of the container, for example a polymeric material such as a polyester, EVA or a modified polyethylene. The polymer material of the heat-sealable layer should soften to a sufficient

extent that its viscosity becomes low enough to allow adequate wetting for it to adhere to the surface to which it is being bonded. The heat-seal bond is effected by heating to soften the polymer material of the heat-sealable layer, and optionally applying pressure, without melting (or otherwise affecting the structure or compromising the structural integrity of) 5 the substrate layer and/or the shrinkable layer. Thus, the polymer of the heat-sealable layer should begin to soften at a temperature such that the heat-seal bond can be formed at a temperature which is less than the melting temperature of the substrate layer or the shrinkable layer. In one embodiment, the polymer of the heat-sealable layer should begin to soften at a temperature such that the heat-seal bond can be formed at a temperature 10 which is between about 5 and 50°C below, preferably between about 5 and 30°C below, and preferably at least about 10°C below the melting temperature of the polymer material of the substrate layer or the shrinkable layer.

The heat-sealable layer suitably comprises a polyester resin; particularly a copolyester 15 resin derived from one or more dicarboxylic acid(s) or their lower alkyl (up to 14 carbon atoms) diesters with one or more glycol(s), particularly an aliphatic or cycloaliphatic glycol, preferably an aliphatic glycol, and more preferably an alkylene glycol. Suitable dicarboxylic acids include aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, phthalic acid, or 2,5-, 2,6- or 2,7-naphthalenedicarboxylic acid, and 20 aliphatic dicarboxylic acids such as succinic acid, sebacic acid, adipic acid, azelaic acid, suberic acid or pimelic acid. Suitable glycol(s) include aliphatic diols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 2,2-dimethyl-1,3-propane diol, neopentyl glycol and 1,6-hexane diol, and cycloaliphatic diols such as 1,4-cyclohexanedimethanol and 1,4-cyclohexane 25 diol. Ethylene glycol or 1,4-butanediol is preferred.

Preferably, the heat-sealable layer comprises a copolyester derived from at least two dicarboxylic acids. Formation of the copolyester is conveniently effected in known manner by condensation, or ester-interchange, at temperatures generally up to 275°C.

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In a preferred embodiment, the copolyester of the heat-sealable layer comprises an aromatic dicarboxylic acid and an aliphatic dicarboxylic acid. A preferred aromatic dicarboxylic acid is terephthalic acid. Preferred aliphatic dicarboxylic acids are selected

from sebacic acid, adipic acid and azelaic acid. The concentration of the aromatic dicarboxylic acid present in the copolyester is preferably in the range from 45 to 80, more preferably 50 to 70, and particularly 55 to 65 mole % based on the dicarboxylic acid components of the copolyester. The concentration of the aliphatic dicarboxylic acid present  
5 in the copolyester is preferably in the range from 20 to 55, more preferably 30 to 50, and particularly 35 to 45 mole % based on the dicarboxylic acid components of the copolyester. Particularly preferred examples of such copolymers are (i) copolymers of azelaic acid and terephthalic acid with an aliphatic glycol, preferably ethylene glycol; (ii)  
10 copolymers of adipic acid and terephthalic acid with an aliphatic glycol, preferably ethylene glycol; and (iii) copolymers of sebacic acid and terephthalic acid with an aliphatic glycol, preferably butylene glycol. Preferred polymers include a copolymer of sebacic acid/terephthalic acid/butylene glycol (preferably having the components in the relative molar ratios of 45-55/55-45/100, more preferably 50/50/100) having a glass transition point ( $T_g$ ) of -30°C and a melting point ( $T_m$ ) of 117°C, and a copolymer of  
15 azelaic acid/terephthalic acid/ethylene glycol (preferably having the components in the relative molar ratios of 40-50/60-50/100, more preferably 45/55/100) having a  $T_g$  of -15°C and a  $T_m$  of 150°C.

In an alternative embodiment, the copolyester of the heat-sealable layer is derived from an  
20 aliphatic diol and a plurality of aromatic dicarboxylic acids, particularly terephthalic acid and isophthalic acid. A preferred copolyester is derived from ethylene glycol, terephthalic acid and isophthalic acid. The preferred molar ratios of the terephthalic acid component to the isophthalic acid component are in the range of from 50:50 to 90:10, preferably in the range from 65:35 to 85:15. In a preferred embodiment, the copolyester is a copolyester of  
25 ethylene glycol with about 82 mole % terephthalate and about 18 mole % isophthalate.

In a further alternative embodiment, the heat-sealable layer comprises a copolyester derived from an aliphatic diol and a cycloaliphatic diol with one or more, preferably one, dicarboxylic acid(s), preferably an aromatic dicarboxylic acid. Typical polyesters which  
30 provide satisfactory heat-sealable properties include copolymers of terephthalic acid with an aliphatic diol and a cycloaliphatic diol, especially ethylene glycol and 1,4-cyclohexanedimethanol. The preferred molar ratios of the cycloaliphatic diol to the aliphatic diol are in the range from 10:90 to 60:40, preferably in the range from 20:80 to

40:60, and more preferably from 30:70 to 35:65. In a preferred embodiment the copolyester is a copolyester of terephthalic acid with about 33 mole % 1,4-cyclohexane dimethanol and about 67 mole % ethylene glycol. An example of such a polymer is PETG<sup>TM</sup>6763 (Eastman) which comprises a copolyester of terephthalic acid, about 33% 5 1,4-cyclohexane dimethanol and about 67% ethylene glycol and which is always amorphous. In an alternative embodiment of the invention, the heat-sealable layer may comprise butane diol in place of ethylene glycol.

The copolyester of the heat-sealable layer is preferably a polymer which is amorphous or 10 substantially amorphous, i.e. non-crystalline. In a preferred embodiment, the amorphous polymer of the heat-sealable layer has a glass transition temperature (Tg) of at least -40°C, preferably at least 70°C and more preferably at least 80°C.

The thickness of the heat-seal layer is generally between about 1 and 30% of the thickness 15 of the substrate layer. The heat-sealable layer may have a thickness of up to about 50 µm, preferably up to about 25µm, more preferably up to about 15µm, more preferably up to about 10µm, more preferably between about 0.5 and 6µm, and more preferably between about 0.5 and 4µm. A thicker heat-sealable layer will generally form a stronger heat-seal bond, which may result in tearing of the film in opening.

20 Formation of the heat-sealable layer on the substrate layer may be effected by conventional techniques, for example by coating (generally off-line coating) or casting the polymer of the heat-sealable layer onto a pre-formed substrate layer. Formation of the heat-sealable layer and the substrate may also be effected by co-extrusion as is well-known in the art and 25 described herein. The coextruded sheet is stretched to effect molecular orientation of the substrate, and preferably heat-set, as herein before described. For most polymers used in the heat-sealable layer, the conditions applied for stretching the substrate layer generally induce partial crystallisation of the heat-sealable polymer and it is therefore preferred to heat set under dimensional restraint at a temperature selected to develop the desired 30 morphology of the heat-setting layer. In general, by effecting heat-setting at a temperature below the crystalline melting temperature of the heat-sealable polymer and permitting or causing the composite to cool, the heat-sealable polymer will remain essentially crystalline. Heat-setting at a temperature greater than the crystalline melting temperature of

the heat-sealing polymer, will produce an essentially amorphous heat-sealable polymeric layer. Thus, heat-setting a composite sheet comprising a polyester substrate and a copolyester heat-sealable layer at a temperature within a range of from 175 to 200°C generally yields a substantially crystalline heat-sealable layer. Using a temperature of from 5 200 to 250°C generally yields an essentially amorphous heat-sealable layer. Certain polymers suitable for use in a heat-sealable layer, such as the PETG referenced above, remain amorphous at all times.

In one embodiment of the invention, the composite structure comprising the substrate layer 10 and the heat-sealable layer may be provided by biaxially-oriented polyester films having a heat-sealable layer which are commercially available as MYLAR® OL film or MYLAR® WOL film (including grades OL, OL2, OL12, OL13, WOL and WOL12; DuPont Teijin Films). Mylar OL is a dual ovenable film which provides peelable seals to polar materials such as amorphous polyester (APET, also PETG), semicrystalline polyester (CPET), 15 polyester coated paperboard and polyvinylchloride (PVC). The heat-seal bond to the container is generally effected in the range from about 140 to about 200°C.

In an alternative embodiment of the invention, the composite structure comprising the substrate layer and the heat-sealable layer may be provided by biaxially-oriented polyester 20 films having an EVA heat-sealable layer which are commercially available as MYLAR® RL film (including grades RL42, RL43; DuPont Teijin Films). Mylar RL is a microwaveable film which provides peelable seals to polypropylene, polystyrene and polyethylene and also to polar materials such as APET, CPET, PVC and PVdC. The heat-seal bond to the container is generally effected in the range from about 120 to about 160°C.

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#### The Shrinkable Layer

The shrinkable layer is a self-supporting film or sheet by which is meant a film or sheet capable of independent existence in the absence of a supporting base. The shrinkable layer comprises any suitable polymeric material provided that it satisfies the requirements of a 30 degree of shrinkage in a first dimension of about 10 to 80%, and preferably about 50 to 80%, over the temperature range 55 to 100°C, and a ratio of shrinkage at 100°C in said first dimension relative to a second, orthogonal dimension in the range from about 1:1 to 10:1, preferably about 2:1 to 8:1, and more preferably from about 3:1 to 7:1. Typically, the

shrinkage in one dimension is about 4:1, for instance one dimension of the film shrinks by about 75% of its size while the orthogonal dimension remains unchanged.

The shrinkable layer preferably comprises thermoplastic polymeric material. Such  
5 materials include a homopolymer or copolymer of a 1-olefin, such as ethylene, propylene and but-1-ene, polyamides, polycarbonates, polyesters (including copolymers), PVC,

PVA, polystyrenes, polyacrylates, celluloses and nylon (including nylon 6 and nylon 6,6).

Particularly preferred is a polyester material, and particularly a synthetic linear polyester.

10 The synthetic linear polyesters useful for formation of the shrinkable layer may be obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters, e.g. terephthalic acid, isophthalic acid, phthalic acid, 2,5-, 2,6- or 2,7-naphthalenedicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, 4,4'-diphenyldicarboxylic acid,

hexahydro-terephthalic acid or 1,2-bis-p-carboxyphenoxyethane (optionally with a

15 monocarboxylic acid, such as pivalic acid) with one or more glycols, particularly an aliphatic or cycloaliphatic glycol, e.g. ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol and 1,4-cyclohexanediethanol. Aromatic dicarboxylic acids are preferred. Aliphatic glycols are preferred.

20 In one embodiment, the polyester of the shrinkable layer is selected from polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), and preferably from polyethylene terephthalate.

In a preferred embodiment, the shrinkable layer comprises a copolyester of terephthalic  
25 acid (TPA) and isophthalic acid (IPA) with one or more diols selected from the group consisting of aliphatic and cycloaliphatic diols. Preferably, the molar ratios of the isophthalate polyester units to the terephthalate polyester units are from 1 to 40 mol % isophthalate and from 99 to 60 mol % terephthalate, preferably from 15 to 20 mol % isophthalate and from 85 to 80 mol % terephthalate. The terephthalic acid/isophthalic acid

30 copolyester may be obtained by condensation polymerisation of terephthalic acid and isophthalic acid with one or more, and preferably one, diol as set out above, preferably an aliphatic diol, more preferably ethylene glycol. In a particularly preferred embodiment, the

shrinkable layer comprises a copolyester comprising substantially 18 mol % ethylene isophthalate and 82 mol % ethylene terephthalate.

In an alternative embodiment, the shrinkable layer comprises a copolymer of terephthalic acid, dihydroxyethyl azelieic acid and ethylene glycol, preferably wherein the dicarboxylic acid components of the copolymer are in a molar ratio of about 90-99% terephthalic acid and about 1-10% dihydroxyethyl azelieic acid, particularly about 95% terephthalic acid and about 5% dihydroxyethyl azelieic acid.

10 The shrinkable layer may itself comprise a monolayer or a multilayer structure, particularly an ABA type structure, particularly where the core layer is a layer comprising a polymer as described above in respect of the preferred embodiment. In such an ABA-type structure, the A layers preferably comprise a polyester or copolyester as described herein, particularly a copolyester of terephthalic acid with about 30-35 mole %, preferably about 15 33 mole % 1,4-cyclohexane dimethanol and about 65-70 mole %, preferably about 67 mole % ethylene glycol.

The thickness of the shrinkable layer is generally in the range of about 10 to about 100 µm, preferably about 25 µm to about 75 µm, and typically about 50 µm.

20 The shrinkable layer may be produced in accordance with the conventional film-forming procedures already described herein. In the preferred embodiment described above, the shrinkable layer is stretched only in one direction and not heat-set. Conveniently, the film is stretched only in the transverse direction. As noted above, stretching is effected to an extent determined by the nature of the polymer. For example, PET is usually stretched so that the dimension of the oriented film in the direction of stretching is from about 2 to 8 times, preferably from about 2 to about 5 times, and more preferably between about 3 and 25 4 times its original dimension.

30 According to a further aspect of the present invention there is provided a process for the production of a multi-layer film which comprises the steps of:  
(i) forming a polymeric film substrate and providing on a first surface thereof a heat-sealable layer;

- (ii) forming a shrinkable layer of polymeric film having a degree of shrinkage in a first dimension of about 10-80% over the temperature range 55 to 100°C and a ratio of shrinkage at 100° C in said first dimension relative to a second, orthogonal dimension in the range from 1:1 to 10:1; and
- 5 (iii) laminating said shrinkable layer onto a second surface of said substrate.

The pre-formed shrinkable layer is applied to the substrate/heat-seal layer multi-layer film, prepared as herein described, using an adhesive in a conventional lamination technique. The lamination stage uses conventional laminating equipment and adhesives.

10

The adhesives suitable for use in preparing the films of this invention are well-known to those skilled in the art, and include epoxy-, polyurethane- or acrylic-based one- or two-part systems. The adhesive may be solvent-based (including water-based) or solvent-free. The particular adhesive chosen will depend on the compositions and the types of layers 15 that are present in the film. Generally, excellent bond strengths can be obtained with high-performance two-component isocyanate adhesives such as Herbert's EPS 74/KN75. Solvent-free adhesives, such as Herbert's 1K-LF 190X3 or Herbert's 2K-LF 541/Hardener 110 may also be used. It is preferable to use solvent-free adhesives for the construction of the laminate as this reduces exposure of the shrinkable layer to any unnecessary thermal 20 cycles.

Prior to lamination of the pre-formed shrinkable layer onto the substrate, the exposed surface of the substrate may, if desired, be subjected to a chemical or physical surface-modifying treatment to improve the bond between that surface and the subsequently 25 applied pre-formed shrinkable layer. A preferred treatment, because of its simplicity and effectiveness, which is particularly suitable for the treatment of a polyolefin substrate, is to subject the exposed surface of the substrate to a high voltage electrical stress accompanied by corona discharge. Alternatively, the substrate may be pretreated with an agent known in the art to have a solvent or swelling action on the substrate polymer. Examples of such 30 agents, which are particularly suitable for the treatment of a polyester substrate, include a halogenated phenol dissolved in a common organic solvent e.g. a solution of p-chloro-m-cresol, 2,4-dichlorophenol, 2,4,5- or 2,4,6-trichlorophenol or 4-chlororesorcinol in acetone or methanol.

The preferred treatment by corona discharge may be effected in air at atmospheric pressure with conventional equipment using a high frequency, high voltage generator, preferably having a power output of from 1 to 20 kw at a potential of 1 to 100 kv. Discharge is 5 conventionally accomplished by passing the film over a dielectric support roller at the discharge station at a linear speed preferably of 1.0 to 500 m per minute. The discharge electrodes may be positioned 0.1 to 10.0 mm from the moving film surface.

One or more of the layers of the polymeric film may conveniently contain any of the 10 additives conventionally employed in the manufacture of polymeric films. Thus, agents such as cross-linking agents, dyes, pigments, voiding agents, lubricants, anti-oxidants, radical scavengers, UV absorbers, thermal stabilisers, anti-blocking agents, surface active agents, slip aids, optical brighteners, gloss improvers, prodegradents, viscosity modifiers and dispersion stabilisers may be incorporated as appropriate. In particular, a layer may 15 comprise a particulate filler which can improve handling and windability during manufacture. The particulate filler may, for example, be a particulate inorganic filler or an incompatible resin filler or a mixture of two or more such fillers.

By an "incompatible resin" is meant a resin which either does not melt, or which is 20 substantially immiscible with the polymer, at the highest temperature encountered during extrusion and fabrication of the film. The presence of an incompatible resin usually results in a voided layer, by which is meant that the layer comprises a cellular structure containing at least a proportion of discrete, closed cells. Suitable incompatible resins include 25 polyamides and olefin polymers, particularly a homo- or co-polymer of a mono-alpha-olefin containing up to 6 carbon atoms in its molecule. Preferred materials include a low or high density olefin homopolymer, particularly polyethylene, polypropylene or poly-4-methylpentene-1, an olefin copolymer, particularly an ethylene-propylene copolymer, or a mixture of two or more thereof. Random, block or graft copolymers may be employed.

30 Particulate inorganic fillers include conventional inorganic fillers, and particularly metal or metalloid oxides, such as alumina, silica (especially precipitated or diatomaceous silica and silica gels) and titania, calcined china clay and alkaline metal salts, such as the carbonates and sulphates of calcium and barium. The particulate inorganic fillers may be of the

voiding or non-voiding type. Suitable particulate inorganic fillers may be homogeneous and consist essentially of a single filler material or compound, such as titanium dioxide or barium sulphate alone. Alternatively, at least a proportion of the filler may be heterogeneous, the primary filler material being associated with an additional modifying 5 component. For example, the primary filler particle may be treated with a surface modifier, such as a pigment, soap, surfactant coupling agent or other modifier to promote or alter the degree to which the filler is compatible with the substrate layer polyester.

Preferred particulate inorganic fillers include titanium dioxide and silica.

10

Titanium dioxide particles may be of anatase or rutile crystal form. The titanium dioxide particles preferably comprise a major portion of rutile, more preferably at least 60% by weight, particularly at least 80%, and especially approximately 100% by weight of rutile. The particles can be prepared by standard procedures, such as the chloride process or the 15 sulphate process. The titanium dioxide particles may be coated, preferably with inorganic oxides such as aluminium, silicon, zinc, magnesium or mixtures thereof. Preferably the coating additionally comprises organic compound(s), such as fatty acids and preferably alkanols, suitably having from 8 to 30, preferably from 12 to 24 carbon atoms. Polydiorganosiloxanes or polyorganohydrogensiloxanes, such as polydimethylsiloxane or 20 polymethylhydrogensiloxane are suitable organic compounds. The coating is suitably applied to the titanium dioxide particles in aqueous suspension. The inorganic oxides are precipitated in aqueous suspension from water-soluble compounds such as sodium aluminate, aluminium sulphate, aluminium hydroxide, aluminium nitrate, silicic acid or sodium silicate. The coating layer on the titanium dioxide particles is preferably in the 25 range from 1 to 12% of inorganic oxides, and preferably in the range from 0.5 to 3% of organic compound, by weight based upon the weight of titanium dioxide.

The inorganic filler should be finely-divided, and the volume distributed median particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the 30 particles, read on the cumulative distribution curve relating volume % to the diameter of the particles - often referred to as the "D(v,0.5)" value) thereof is preferably in the range from 0.01 to 5  $\mu\text{m}$ , more preferably 0.05 to 1.5  $\mu\text{m}$ , and particularly 0.15 to 1.2  $\mu\text{m}$ .

The size distribution of the inorganic filler particles is also an important parameter, for example the presence of excessively large particles can result in the film exhibiting unsightly 'speckle', i.e. where the presence of individual filler particles in the film can be discerned with the naked eye. It is preferred that none of the inorganic filler particles 5 incorporated into the substrate layer should have an actual particle size exceeding 30 µm. Particles exceeding such a size may be removed by sieving processes which are known in the art. However, sieving operations are not always totally successful in eliminating all particles greater than a chosen size. In practice, therefore, the size of 99.9% by number of the inorganic filler particles should not exceed 30 µm, preferably should not exceed 20 µm, 10 and more preferably should not exceed 15 µm. Preferably at least 90%, more preferably at least 95% by volume of the inorganic filler particles are within the range of the volume distributed median particle diameter  $\pm$  0.8 µm, and particularly  $\pm$  0.5 µm.

Particle size of the filler particles may be measured by electron microscope, coulter 15 counter, sedimentation analysis and static or dynamic light scattering. Techniques based on laser light diffraction are preferred. The median particle size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile.

20 The components of the composition of a layer may be mixed together in a conventional manner. For example, by mixing with the monomeric reactants from which the layer polymer is derived, or the components may be mixed with the polymer by tumble or dry blending or by compounding in an extruder, followed by cooling and, usually, comminution into granules or chips. Masterbatching technology may also be employed.

25

In one embodiment, the film of the present invention is optically clear, preferably having a % of scattered visible light (haze) of <10%, preferably <6%, more preferably <3.5 % and particularly <2%, measured according to the standard ASTM D 1003. In this embodiment, 30 filler is typically present in only small amounts, generally not exceeding 0.5% and preferably less than 0.2% by weight of a given layer.

In an alternative embodiment, the film is opaque and highly filled, preferably exhibiting a Transmission Optical Density (TOD) (Sakura Densitometer; type PDA 65; transmission

mode) in the range from 0.1 to 2.0, more preferably 0.2 to 1.5, more preferably from 0.25 to 1.25, more preferably from 0.35 to 0.75 and particularly 0.45 to 0.65. The film is conveniently rendered opaque by incorporation into the polymer blend of an effective amount of an opacifying agent. Suitable opacifying agents include an incompatible resin 5 filler, a particulate inorganic filler or a mixture of two or more such fillers, as hereinbefore described. The amount of filler present in a given layer is preferably in the range from 1% to 30%, more preferably 3% to 20%, particularly 4% to 15%, and especially 5% to 10% by weight, based on the weight of the layer polymer.

- 10 The surface of an opaque film preferably exhibits a whiteness index, measured as herein described, in the range from 60 to 120, more preferably 80 to 110, particularly 90 to 105, and especially 95 to 100 units.

The surface of the substrate in contact with the heat sealable layer is referred to herein as 15 the primary side. The side of the substrate opposite to the side which is in contact with the heat-sealable layer is referred to herein as the secondary side. The secondary side of the substrate may have thereon one or more further polymeric layers or coating materials. Any coating of the secondary side is preferably performed "in-line".

- 20 In one embodiment, the additional coating on the secondary side may comprise a "slip coating" in order to improve the handling and windability of the film, particularly when the film substrate is a PET polyester substrate. A suitable slip coating may be, for instance a discontinuous layer of an acrylic and/or methacrylic polymeric resin optionally further comprise a cross-linking agent, such as described in EP-A-0408197, the disclosure of 25 which is incorporated herein by reference. An alternative slip coating may comprise a potassium silicate coating, for instance as disclosed in US Patent Nos. 5925428 and 5882798, the disclosures of which are incorporated herein by reference.

A polymeric film according to the invention is useful for sealing or providing a lid on a 30 container, such as a thermoformed tray, thermoformed bowl or blow-moulded bottle. The container may be formed of polyester, such as polyethylene terephthalate, or of polypropylene, polystyrene, or may be PVDC coated, or may be glass. A film according to the invention is particularly suitable for use as a lid for an APET/CPET container,

especially a thermoformed tray, which is suitable for packaging food or drink. Other suitable types of container include a foil tray (particularly an aluminium foil tray), a metallised tray and a tray formed from PET-coated cartonboard or paperboard. Of particularly utility are trays formed from metallised (particularly flash-metallised) PET 5 cartonboard. For example, the tray may be produced from PET which has been metallised to an optical density in the range of about 0.01 to 4.0 and which is laminated to cartonboard. In one embodiment, the tray is a susceptor tray made from materials such as those disclosed in GB-A-2280342, EP-A-0563442 or GB-A-2250408, or is a susceptor tray produced in accordance with the disclosures of these documents, which are incorporated 10 herein by reference.

The invention further provides a sealed container comprising a receptacle containing food or drink, and a lid formed from a polymeric film as defined herein.

15 The sealed container is produced by techniques well-known to those skilled in the art. Once the food to be packaged has been introduced into the container, the heat-sealable film lid is affixed using temperature and/or pressure using conventional techniques and equipment. The multilayer film lid is placed on the container such that the heat-sealable layer is in contact with the surfaces of the container and the shrinkable layer is the 20 outermost surface of the film lid.

It is preferred that a portion of the film lid in contact with the container forms a stronger heat-seal bond with the container than that formed between the container and the remainder of the film lid in contact with the container. In this way, the film lid is more 25 strongly attached to the container during the cooking cycle and remains attached to one side of the container during the self-peeling process, thereby ensuring that the film lid peels back on itself during the cooking cycle. Thus, for a quadrilateral container, such as a rectangular or square container, it is preferred that the heat-seal bond on one side of the container is stronger than the heat-seal bond on the other three sides. For a circular or oval 30 container, it is preferred that one sectional arc of the substantially circular or elliptical circumference of the open end of the container, for instance an arc comprising less than about 180°, preferably less than about 90°, preferably less than about 60°, and preferably less than about 45°C of the circumference, has a stronger heat-seal bond than the remaining

section of the circumference. Varying strengths of heat-seal bond may be achieved by forming different sections of the heat-seal bond between the film lid and the container at different temperatures. Thus, for a quadrilateral tray for instance, it is preferred that the heat-sealing equipment is configured such that three of the sides of the heat-seal head 5 operate at a temperature in the range of about 110 to 150°C, preferably at about 130°C, and the fourth side operates at a temperature in the range of about 150 to 200°C, preferably about 170°C.

In a particularly preferred embodiment, the film lid is folded over the flange on this fourth 10 side of the container and the heat-seal head also forms a heat-seal bond between the film lid and the underside of the flange of the container on this fourth side. Ideally the film would be folded over the flange on the fourth side and sealed top and bottom.

In a further embodiment, the bond between the film lid and one side of the container may 15 be enhanced by mechanical means, such as crimping or stapling, in order to ensure that the lid peels back on itself during the cooking cycle.

The sealed container is particularly suitable for use as a receptacle for ready prepared convenience foods which are intended to be warmed in a microwave oven. However, the 20 invention is also applicable for ready-prepared meals which are intended to be warmed in any other type of oven, such as a conventional convection oven, a direct radiation oven and a forced hot air oven.

The invention is illustrated by figures 1 and 4 herein, in which:

25

Figure 1 is a sectional view of the film (1) according to the present invention comprising a shrinkable layer (2), a substrate layer (3) and a heat-sealable layer (4).

Figure 2 is a sectional view of the film (1) after having been heat-sealed to the container 30 (5) having food product (6) therein. The heat-seal layer (4) is in contact with the container with the shrinkable layer (2) uppermost.

Figure 3 is a view of the container (5) having walls (a), (b), (c) and (d). In a preferred embodiment of the invention, the film lid is heat sealed to the tray such that the heat-sealed lid has a stronger bond to the upper surface of wall (a) than to sides (b), (c) and (d).

- 5 Figure 4 is a sectional view of container (5) having walls (a), (b), (c) and (d) (walls (b) and (d) not shown) and having at the top of walls (a) and (c) flanges (6a) and (6c). According to a preferred embodiment of the invention, film (1) is heat-sealed to both the upper and lower surfaces of flange (6a).
- 10 The following test methods may be used to determine certain properties of the polymeric film:
  - (i) Wide angle haze is measured using a Hazegard System XL-211, according to ASTM D 1003-61.
  - (ii) Whiteness index is measured using a Colorgard System 2000; Model/45
- 15 (manufactured by Pacific Scientific) based on the principles described in ASTM D313.
- (iii) Heat-seal strength is measured as follows. The laminated film is sealed, by means of the heat-sealable layer, to a standard APET/CPET tray using a Microseal PA 201 (obtained from Packaging Automation Ltd, England) tray sealer at a temperature of
- 20 180°C, and pressure of 80 psi for two seconds. Strips of the sealed film and tray are cut out at 90° to the seal, and the load required to pull the seal apart measured using an Instron operating at a crosshead speed of 0.2 mmmin<sup>-1</sup>. The procedure is generally repeated 4 times, and a mean value of 5 results calculated.
- (iv) Shrinkage at a given temperature is measured by placing the sample in a heated water bath at that temperature for 30 seconds. The shrinkage behaviour over the range 55 to 100 °C is assessed using a number of film samples at different temperatures over this range, generally at intervals of 5-10 °C.

The invention is further illustrated by the following examples. It will be appreciated that

30 the examples are for illustrative purposes only and are not intended to limit the invention as described above. Modification of detail may be made without departing from the scope of the invention.

**EXAMPLES****Example 1***Preparation of the composite film comprising the substrate and the heat-sealable layer*

- 5 A polymer composition comprising polyethylene terephthalate was extruded and cast onto a cooled rotating drum and stretched in the direction of extrusion to approximately 3 times its original dimensions. The film was passed into a stenter oven at a temperature of 100°C where the film was stretched in the sideways direction to approximately 3 times its original dimensions. The biaxially stretched film was heat-set at about 230°C by conventional  
10 means. The heat-set film was then coated off-line using conventional coating means with a copolyester of azelaic acid/terephthalic acid/ethylene glycol (45/55/100) to give a dry coating thickness of 2 µm. The total film thickness was 20 µm.

*Preparation of the shrinkable layer*

- 15 A polymer composition comprising a copolyester of 18 mol % ethylene isophthalate and 82 mol % ethylene terephthalate was melt-extruded and cast onto a cooled rotating drum. The film was passed into a stenter oven at a temperature of about 90°C where the film was dried and stretched in the sideways direction to approximately 3.8 times its original dimensions. The total thickness of the final film was 50 µm.

20

*Preparation of the laminated film according to the present invention*

- The multilayer laminated film of the present invention is prepared by laminating together the shrinkable film and the substrate/heat-sealable composite film, prepared as described above. The lamination is effected according to conventional techniques using a First  
25 Laminator machine (Taisei Laminator Company Ltd.). The adhesive used in the lamination was Novacote™ 2525/3 two-part adhesive.

*Preparation of the sealed container according to the present invention*

- The multilayer film prepared in accordance with the above procedure was heat-sealed to a  
30 microwave susceptor tray (Trykko Pack A/S, Denmark), using a Sentinel Heat Sealer (Packaging Industries, USA) at a temperature of 130°C and a pressure of 40 psi for 0.5 sec on three sides and a temperature of 160°C and a pressure of 80 psi for 0.5 seconds on the fourth side of the tray.

The bond strength of the heat-seal was measured, using the procedure described above, to be 500 gms/25mm<sup>2</sup>.

The sealed container was placed in an 800W microwave oven for 2 minutes, and removed  
5 from the oven at the end of the heating cycle. The film lid of the container had peeled back from three sides of the container and remained attached to the fourth side.

### **Example 2**

A laminated film was prepared in accordance with Example 1 except that the shrinkable  
10 layer was prepared as follows:

A polymer composition comprising a copolyester of 18 mol% ethylene isophthalate and 82 mol% ethylene terephthalate was co-extruded with a copolyester of terephthalic acid/1,4-cyclohexane dimethanol/ethylene glycol (100/33/67) to form an ABA structure, the core layer (B) being the ethylene isophthalate/ethylene terephthalate copolyester. The film was  
15 passed into a stenter oven at a temperature of about 90°C where the film was stretched in the sideways direction to approximately 3.8 times its original dimensions.

### **Example 3**

A laminated film was prepared in accordance with Example 1 except that the composite  
20 structure of the substrate and heat-sealable layer was prepared as follows:

A polymer composition comprising polyethylene terephthalate (substrate layer polymer) was co-extruded with a copolyester comprising terephthalic acid/isophthalic acid/ethylene glycol (82/18/100) (heat-sealable layer polymer), cast onto a cooled rotating drum and stretched in the direction of extrusion to approximately 3 times its original dimensions.  
25 The film was passed into a stenter oven at a temperature of 100°C where the film was stretched in the sideways direction to approximately 3 times its original dimensions. The biaxially-stretched film was heat-set at a temperature of about 230°C by conventional means. The total thickness of the final film was 23 µm; the heat sealable layer was approximately 4 µm thick.

CLAIMS

1. A film according to the present invention, there is provided a multi-layer laminated polymeric film comprising a substrate layer having on one side thereof a heat-sealable peelable layer and having on the opposite side thereof a shrinkable layer, wherein said shrinkable layer has a degree of shrinkage in a first dimension of about 10-80% over the temperature range 55 to 100°C, and a ratio of shrinkage at 100°C said first dimension relative to a second, orthogonal dimension in the range of 1:1 to 10:1.  
10
2. A film according to claim 1 wherein the substrate comprises polyester.
3. A film according to claim 1 wherein the substrate comprises poly(ethylene terephthalate).
- 15 4. A film according to any preceding claim wherein the shrinkable layer comprises a copolyester of terephthalic acid (TPA) and isophthalic acid (IPA) with one or more diols selected from the group consisting of aliphatic and cycloaliphatic diols.
- 20 5. A film according to claim 4 wherein said copolyester comprises isophthalate polyester units and terephthalate polyester units in molar ratios of from 1 to 40 mol % isophthalate and from 99 to 60 mol % terephthalate.
- 25 6. A film according to claim 4 or 5 wherein the copolyester comprises ethylene glycol.
7. A film according to claim 4, 5 or 6 wherein the shrinkable layer comprises a copolyester comprising substantially 18 mol % ethylene isophthalate and 82 mol % ethylene terephthalate.
- 30 8. A film according to any of claims 1 to 7 wherein the heat-sealable peelable layer comprises a copolyester of an aromatic dicarboxylic acid, an aliphatic dicarboxylic acid and a glycol.

9. A film according to claim 8 wherein said copolyester of the heat-sealable peelable layer comprises terephthalic acid, azelaic acid and ethylene glycol.
10. A film according to claim 9 wherein said copolyester is a copolyester of ethylene glycol with about 55% terephthalic acid and about 45% azelaic acid.  
5
11. A film according to any of claims 1 to 7 wherein the heat-sealable peelable layer comprises a copolyester derived from an aliphatic diol, a cycloaliphatic diol and a dicarboxylic acid.  
10
12. A film according to claim 11 wherein the heat-sealable peelable layer comprises a copolyester of terephthalic acid with ethylene glycol and 1,4-cyclohexanedimethanol.
- 15 13. A film according to claim 12 wherein the heat-sealable peelable layer comprises a copolyester of terephthalic acid with ethylene glycol and 1,4-cyclohexanedimethanol wherein the molar ratio of 1,4-cyclohexanedimethanol to ethylene glycol is in the range from 20:80 to 40:60.  
20
14. A film according to claim 13 wherein the heat-sealable peelable layer comprises a copolyester of terephthalic acid with about 33 mole % 1,4-cyclohexane dimethanol and about 67 mole % ethylene glycol.
15. A sealed container comprising a receptacle containing food or drink, and a lid formed from a polymeric film according to any of claims 1 to 14.  
25
16. A process for the production of a multi-layer film which comprises the steps of:
  - (i) forming a polymeric film substrate and providing on a first surface thereof a heat-sealable peelable layer;
  - 30 (ii) forming a shrinkable layer of polymeric film having a degree of shrinkage in one dimension of about 10-80% over the temperature range 55 to 100°C and a ratio of shrinkage at 100°C in said first dimension to a second, orthogonal dimension in the range from 1:1 to 10:1; and

(iii) laminating said shrinkable layer onto a second surface of said substrate.

17. A process according to claim 16 wherein the components of the multilayer film are as set out in any of claims 1 to 14.

1/1

FIG. 1

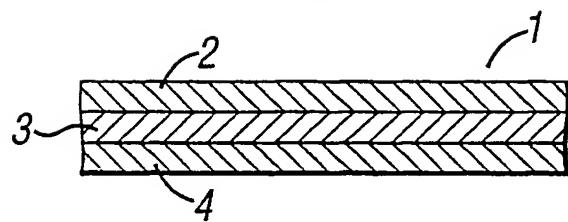


FIG. 2

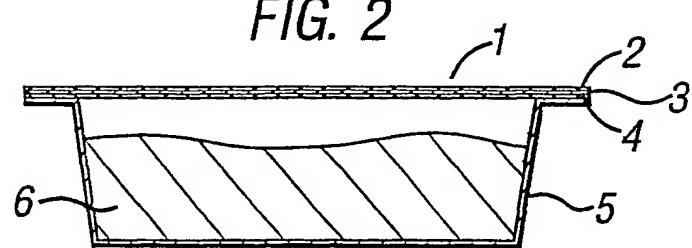


FIG. 3

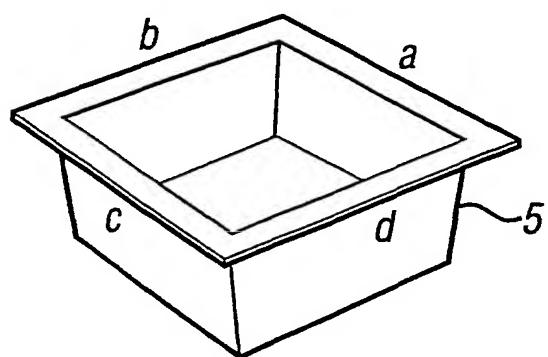
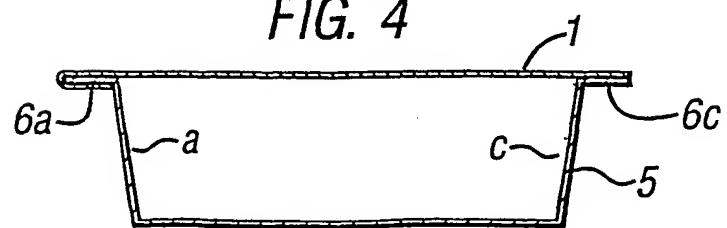


FIG. 4



## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 01/04295

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B32B27/32 B65D77/20 B32B27/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B65D B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 62982 A (DU PONT) 9 December 1999 (1999-12-09) claims 1,3,5,10 page 3, line 12 - line 29 page 6, line 12 -page 7, line 11 page 9, line 20 - line 25 example 1	1-8, 11-17 9,10
Y	WO 90 07853 A (DU PONT) 12 July 1990 (1990-07-12) claims 1,3-5,14,15,18 page 4, line 33 -page 6, line 7 page 9, line 14 - line 22	9,10
	----- -/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*&\* document member of the same patent family

Date of the actual completion of the international search

19 December 2001

Date of mailing of the international search report

16/01/2002

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## INTERNAL SEARCH REPORT

International Application No  
PCT/GB 01/04295

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 198730 Derwent Publications Ltd., London, GB; Class A17, AN 1987-208865 XP002186099 & JP 62 134261 A (OKURA IND CO LTD), 17 June 1987 (1987-06-17) abstract -----	1-17
A	DATABASE WPI Section Ch, Week 199046 Derwent Publications Ltd., London, GB; Class A92, AN 1990-344516 XP002186100 & JP 02 248244 A (SHOWA ALUMINIUM CO LTD), 4 October 1990 (1990-10-04) abstract -----	1-17

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International Application No.  
PCT/GB 01/04295

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